



Kinetic study of propane aromatization over Zn/HZSM-5 zeolite under conditions of catalyst deactivation using genetic algorithm

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Abstract: The kinetic studies of propane aromatization reaction over Zn/HZSM-5 catalyst at temperature of 500–560 °C and space velocity of 500–2500 cm³ g_{cat}⁻¹ h⁻¹, in a plug flow reactor, under catalyst deactivating conditions were performed. A lumped kinetic model consisting of six lumped components and six reaction steps was proposed to describe the aromatization of propane. The kinetic model involves 18 kinetic parameters and one catalyst deactivation constant. The reaction steps orders were obtained by the power law model. Frequency factors and the apparent activation energies of the reaction steps were calculated based on the Arrhenius equation. An exponential function depending on the time-on-stream was applied for the catalyst deactivation model and the kinetic parameters were calculated *via* a genetic algorithm. The kinetic results indicated that the lumped kinetic model can well estimate the product yields of propane aromatization.

Keywords: kinetic modelling; conversion of propane to aromatics; lump; Zn/HZSM-5 catalyst; deactivation of catalyst.

INTRODUCTION

In the past few decades rapid advances have been seen in the field of transformation of light hydrocarbons to the more valuable products. In this regard, the conversion of light alkanes into aromatics has received considerable attention within the industrial and academic fields. BTX aromatic hydrocarbons, namely, benzene, toluene and xylenes are produced by light alkanes aromatization. BTX aromatic hydrocarbons are considered as valuable intermediates in the chemical and petrochemical applications.^{1–6} The modified medium-pore zeolites ZSM-5 by metals such as zinc,^{7,8} gallium^{9,10} or platinum¹¹ have been chosen as catalysts for different light alkanes aromatization. The incorporation of metal species leads to the additional dehydrogenation activity of the protonic form HZSM-5.^{3–5}

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The aromatization of light alkanes using ZSM-5 catalysts involves three main stages: alkane transformation into alkenes, alkene oligomerization and cracking, and alkene aromatization. The first stage of the alkane transformation includes two mechanisms: the protolytic cracking (monomolecular) and the hydrogen transfer (bimolecular), resulting in smaller olefins and paraffins formation and the transformation into the related olefins, respectively.¹² The second stage of the alkene interconversion proceeds through alkene oligomerization and cracking. The third stage involves the cyclization and the hydrogen transfer steps.¹³⁻¹⁸ The most serious disadvantage of aromatization reactions is the coke formation which contributes to the blockage of the active sites, that leads to the catalyst deactivation. Several studies have investigated the reaction stages of transformation of higher alkenes and also the coke formation.¹⁹⁻²²

Kinetic study is a very useful tool to develop a better understanding of catalytic processes and has been used for the reactor simulation, to predict the products distribution and to optimize the operating conditions. Many authors have investigated the microkinetic approach behind the propane aromatization reaction over ZSM-5 zeolite catalyst in the non-deactivating conditions.^{16,17,23,24} However, a main problem with the detailed kinetic models of catalytic cracking and aromatization, such as the microkinetic model, is the presence of large number of reaction steps and their associated rates constants that must be estimated. Recently, a lumped kinetic model has been developed to avoid such aforementioned problems.²⁵⁻²⁷ The recent developments in genetic algorithms (GAs) have led to a renewed interest within the field of chemical engineering. It plays an important role considering the issues of optimization problems, such as the reactor design,²⁸ the optimization of reaction conditions²⁹ and the estimation of kinetic parameters.³⁰ Although GAs are estimated as expensive, they are employed for providing the global optima and a better solution.

This paper investigates the kinetic studies of the propane aromatization on Zn/HZSM-5 at temperature in the range of 500–560 °C and space velocity of 500–2500 cm³ g_{cat}⁻¹ h⁻¹ along with the deactivating conditions. This lumped kinetic model has been presented in six reaction steps along with six lumped components. An exponential function depending on the time on stream describes the catalyst deactivation model. The optimal solution for the optimization problems has been performed using GA.

EXPERIMENTAL

Catalyst preparation

Na-ZSM-5 zeolite was synthesized by the hydrothermal crystallization using Ludox (30 wt. % SiO₂), sodium aluminate, sodium hydroxide and deionized water in a stainless steel autoclave at 170 °C for 144 h. The resulting crystalline product was washed, dried at 100 °C for 12 h and calcined in static air at 550 °C for 16 h, respectively. In order to convert Na form zeolite to NH₄ form, the ion exchange was carried out twice with ammonium nitrate (1 M)

solution under reflux at 70 °C for 24 h. HZSM-5 was prepared by the calcination of the resulting $\text{NH}_4\text{-ZSM-5}$ at 600 °C in air for 5 h.

Zinc was introduced over HZSM-5 zeolite by the ion exchange and the impregnation methods. Two Zn/HZSM-5 samples were prepared by the ion exchange of HZSM-5 with 0.01 and 0.02 M solution of zinc nitrate at 70 °C, respectively.^{7,31} The samples were filtered, washed with deionized water, dried at 100 °C overnight and calcined at 600 °C on air for 5 h. 3 wt. % of Zn/HZSM-5 zeolite was obtained by the wet impregnation of zinc nitrate on the HZSM-5 in a rotary evaporator. After being impregnated, the product was dried at 100 °C overnight and calcined at 600 °C in air for 5 h, respectively.

Catalyst characterization

The crystalline structure of the impregnated Zn/HZSM-5 sample was characterized by the X-ray diffraction (XRD) measurements. The XRD pattern was recorded on a Panalytical diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, 40 kV, 40 mA) and the 2θ scan range was from 5 to 80° with a 2θ -step of 0.026°.

The crystal size and morphology of the ZSM-5 zeolite were studied by the scanning electron microscopy (SEM) model Vega Tescan. Prior to undertaking SEM images, the sample was coated with gold. The Brunauer–Emmett–Teller (BET) surface area, S_{BET} , the total pore volume, V_p , and the average pore radius, r_p , were measured using nitrogen adsorption isotherm at 77 K.

In order to determine the amount of the coke deposited on the catalyst, the spent catalysts after 21 h time on stream (TOS) were thermally analyzed. The thermal analysis (TG and DTA) using a Bahr, STA504 (Germany) was carried out under static air with the heating rate of 10 °C/min, starting from 50 to 800 °C.

Catalyst performance

The aromatization of propane on the Zn/HZSM-5 zeolite was performed in a vertical fixed bed quartz tubular microreactor (inner diameter (i.d.) = 6 mm, outer diameter (o.d.) = 8 mm), installed in a furnace at the atmospheric pressure. 300 mg of catalyst was loaded in the reactor for each run. The feed, a mixture of propane and nitrogen (50 mol % propane), was introduced by two mass flow controllers (MFCs) from top of the reactor. All runs were carried out at the reaction temperature of 500–560 °C and space velocity of 500–2500 $\text{cm}^3 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$. The catalyst activity and the product selectivity were calculated as a function of time on stream up to about 21 h.

The reaction products were analyzed by an on-line Thermofinnigan gas chromatograph (model No. KAV00109), using Hayesep Q, MolSieve 13X columns and the thermal conductivity detector (TCD) for detection of permanent gases such as nitrogen and Q-plot and the flame ionization detector (FID) for separation of the hydrocarbon products. The reactor outlet pipeline was heated at about 160 °C to avoid heavy products condensation. This experimental set up has been used for the previous work.³² Propane conversion and product selectivity are defined as follows (wt. % is weight percentage of a compound in the hydrocarbon products):

$$\text{Propane conversion, \%} = 100 - \frac{\text{Amount of propane in the hydrocarbon products, wt. \%}}{\text{Amount of propane in the feed, wt. \%}} \quad (1)$$

$$\text{Selectivity of i, \%} = 100 \frac{\text{Amount of compound i in the hydrocarbon products, wt. \%}}{100 - \text{Amount of propane in the hydrocarbon products, wt. \%}} \quad (2)$$

After preparing Zn/HZSM-5 catalysts, propane aromatization reaction over the synthesized catalysts was carried out in the described microreactor. Table S-1 in Supplementary material to this paper shows the propane aromatization behaviour of the synthesized Zn/HZSM-5

catalysts at high temperature of 560 °C and low space velocity of 500 cm³ g_{cat}⁻¹ h⁻¹ conditions (maximum yields of products, wt. %, were obtained in this reaction conditions). According to higher propane conversion, selectivity and yield of aromatics over impregnated Zn/HZSM-5 catalyst, it was considered as a chosen catalyst for characterization and kinetic study.

Kinetic model

Lumped kinetic model. Propane aromatization is a complicated heterogeneous reaction that includes number of reaction species and many reaction steps. As a result, many by-products are formed. To decrease the number of the reaction species, lumping all isomers of the same carbon number into a single component was carried out.²⁵⁻²⁷ The main aim of this study is to develop a lumped kinetic model, by considering the reaction conditions and products distribution of propane aromatization.

A simple kinetic model on the basis of six lumped components was developed. The kinetic scheme displays the main reaction pathways during the propane aromatization. There are six reaction steps in it. They involve converting propane into paraffins and light olefins and transforming these olefins into heavy products and converting them into aromatics and also coke formation from heavy products and aromatics (Fig. 1).

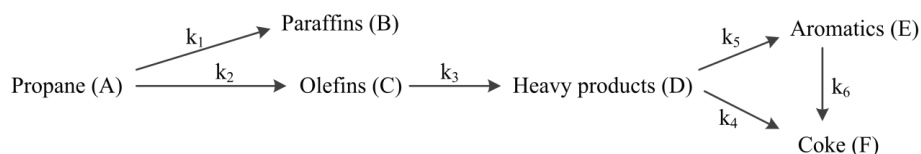


Fig. 1. Kinetic scheme with six lumps for the propane aromatization over Zn/HZSM-5 catalyst.

The reaction products may be classified on the basis of five lumped components: paraffins (B): methane, ethane and butane, olefins (C): ethylene, propylene and butene, heavy products (D): olefin and paraffins with five or more carbons, aromatics (E): benzene, toluene and xylenes, coke (F).

The reaction network was applied according to Nguyen *et al.*¹⁶ work, which is presented in Table I. It is worth noting that the reaction 1 in the reaction network is explained through the reactions (3) and (4) in Table I (hydrogen transfer and protolytic cracking C-C bond). The reaction (2) of the proposed kinetic scheme is defined by the reactions (1)–(4) in Table I, leading to ethylene, propylene and butene products. The reaction (3) in Fig. 1 is explained as

TABLE I. Reaction steps for propane aromatization on the Zn/HZSM-5 zeolite

Reaction	Description
(1) $C_3 \rightarrow C_3^{2-} + H_2$	Protolytic cracking C–H bond of propane on zeolite acid and zinc catalytic sites
(2) $C_3 \rightarrow C_2^{2-} + C_1$	Protolytic cracking C–C bond of propane on zeolite acid and zinc catalytic sites
(3) $C_3 + C_n^{2-} \rightarrow C_3^{2-} + C_n$	Hydrogen transfer between propane and alkenes over zeolite acid sites, $2 \leq n \leq 8$
(4) $C_n^{2-} + C_m^{2-} \rightarrow C_{n+m}^{2-}$	Alkene oligomerization and formation of heavy products on zeolite acid sites, $2 \leq n, m \leq 8, n+m \leq 8$
(5) $C_n^{2-} + 3C_m^{2-} \rightarrow AR + 3C_m$	Heavy products aromatization over zeolite acid and zinc catalytic sites, $6 \leq n, m \geq 2$

the oligomerization. The reaction (5) of the reaction network is considered as the aromatization reaction.

In contrast to low coke yield, it is considered as one lump. In this regard, the prediction of the coke yield is significant for the catalyst deactivation. Furthermore, higher alkenes and aromatics are suggested to be coke precursors in the alkane aromatization over ZSM-5 zeolite.^{20,21} In this kinetic scheme, the coke formation reactions from heavy products and aromatics are counted.

In the kinetic model of the propane aromatization, the total reaction rate of each lump i , represented by R_i , was determined as the sum of the all reaction rates at different steps. The simple power law model is usually used due to the complexity of the catalytic reactions. In the previous studies,^{26,27} the lumped kinetic model was used for the catalytic cracking assuming the first and second-order reactions. In order to improve the precision of the kinetic parameters, the power law model was applied to calculate the rate of each reaction step. Therefore, the reaction rate of each lump i , R_i , was expressed as a function of lump concentration, c_i , the rate constant of reaction step j , k_j , the power of the reaction species concentration j , P_j , and the catalyst activity, a , which are illustrated by Eqs. (S-1)–(S-7) of the Supplementary material.

The following general expression for the deactivation equation by the coke deposition (which considers the concentration of coke precursors) is defined as:

$$-\frac{da}{dt} = \Psi(T, c_i) a^d \quad (3)$$

where $\Psi(T, c_i)$ is the non-separable deactivation function and d is the deactivation order. The term catalyst activity, a , defined in order to describe the catalyst deactivation in the kinetic model as the ratio between the reaction rates at t and zero time on stream:^{33,34}

$$a = \frac{(R_i)_t}{(R_i)_{t=0}} \quad (4)$$

As the product components can bring about coke formation, the independent deactivation equation could be used and the deactivation order equals 1 was assumed.^{35,36} Therefore, the following equation is obtained:

$$-\frac{da}{dt} = \alpha a \quad (5)$$

With integrating from the Eq. (5) gives:

$$a = \exp(-\alpha t) \quad (6)$$

where α is defined as the catalyst deactivation constant, h^{-1} .

Estimation of kinetic parameters

Since diameters ratio of the reactor and catalyst particles, d_r/d_p was in the range of 10–20 (particle fraction between 0.3 and 0.6 mm) and the ratio of the reactor length and catalyst particles diameter, L/d_p was in the range of about 35–65 and also the temperature gradient along the fixed-bed was less than 1 °C, the isothermal plug flow reactor conditions can be considered.^{16,26} Based on the aforementioned matters, the following expressions are determined:

$$\frac{dw_1}{dt} = R_i M_i \quad (7)$$

TABLE II. Numerical parameters used in GA

Parameter	Value
Population size	100
Cross over rate	0.9
Mutation rate	0.05
Number of generation	1000
Selection function	Tournament

$$\tau = \frac{W}{m} = WHSV^{-1} \quad (8)$$

where w_i is the mass fraction of lump i , τ is the space time, h, $WHSV$ is the weight hourly space velocity, h^{-1} , M_i is the average molecular weight of component i , $mol\ g^{-1}$, W is the catalyst weight, g and m is the mass flow rate of the feed, $g\ h^{-1}$. The rate constants are calculated according to the Arrhenius equation:

$$k_j = k_{j,0} \exp\left(\frac{-E_j}{RT}\right) \quad (1 \leq j \leq 6) \quad (9)$$

where $k_{j,0}$, E_j are frequency factor and apparent activation energy of reaction step j , respectively.

In order to solve the set of differential equations, fourth order Runge–Kutta method and MATLAB software as a programming tool were applied. To estimate the kinetic parameters, an objective function was minimized by the genetic algorithm. In this study, an objective function was defined as follows:

$$OF = \sum_{i=1}^b \sum_{s=1}^f (Y_{is} - Y_{is}^{model})^2 \quad (10)$$

where Y is the yield of products, b is the number of lumps and f is the number of experimental runs. The numerical values used in the GA for all optimization runs are shown in Table II.

RESULTS AND DISCUSSION

Catalyst characterization

The XRD pattern confirmed the MFI (Zeolite Framework Type ZSM-Five) structure of the zeolite by the sharp peaks at diffraction angles of 2θ $7.5\text{--}9^\circ$ and $22.5\text{--}24.5^\circ$. The XRD pattern showed that the Zn and ZSM-5 phases were present in the sample (Fig. 2).

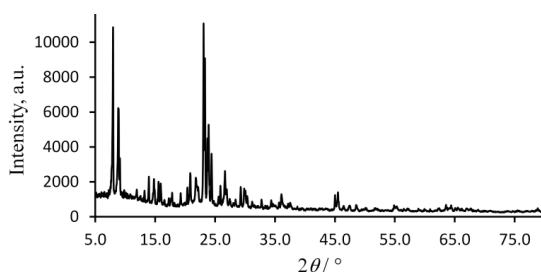


Fig. 2. XRD pattern of the impregnated Zn/HZSM-5 zeolite sample.

The Fig. 3 presents the SEM image of the impregnated Zn/HZSM-5 sample. According to the Fig. 3, the average particle sizes of the impregnated zeolite sample, S , were predicted and are reported in Table III.

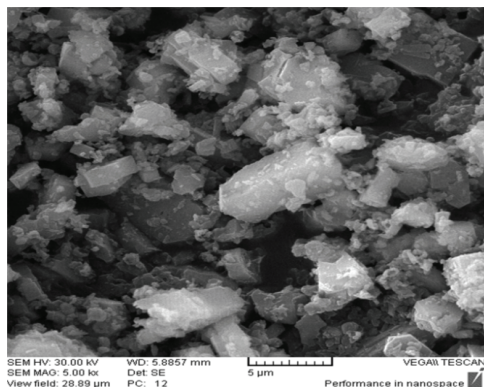


Fig. 3. SEM image of the impregnated Zn/HZSM-5 catalyst.

The physical properties of the impregnated Zn/HZSM-5 catalyst are illustrated in Table III.

TABLE III. Physical properties of impregnated Zn/HZSM-5 sample

Parameter	Value
$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	225
$V_p / \text{cm}^3 \text{g}^{-1}$	0.181
r_p / nm	1.292
$S / \mu\text{m}$	$1 < S < 6$
Si/Al ratio (measured by EDAX)	26

The thermogravimetric (TG) and the differential thermal analysis (DTA) curves of the spent catalyst at the reaction conditions of 560 °C and the space velocity of 500 $\text{cm}^3 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ are shown in the Fig. 4. The weight loss occurs at

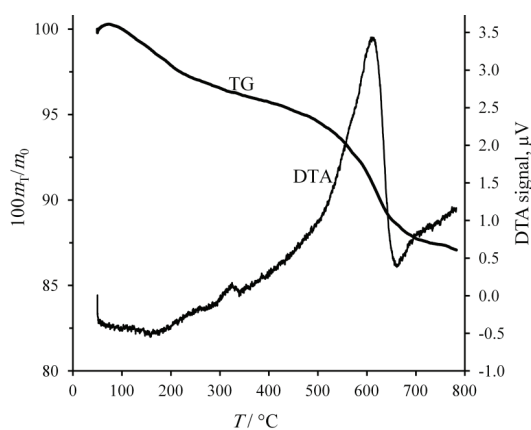


Fig. 4. TG and DTA curves of impregnated Zn/HZSM-5 spent catalyst at 560 °C and space velocity of 500 $\text{cm}^3 \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$.

higher temperature (above 500 °C) and the exothermic DTA peak is observed at 612 °C, which is due to the oxidation of coke deposited on the catalyst (Fig. 4). The thermal analysis results show that for the initial high propane conversion, more coke deposited on the catalyst and consequently more catalyst underwent deactivation.

Kinetic modelling results

All the kinetic parameters such as the apparent activation energies E_j , the pre-exponential factors $k_{j,0}$ and the reaction orders P_j have been estimated by GA as presented in Table IV. The high activation energy values mentioned in Table IV show that all of the reactions are temperature sensitive. In comparison with the values of the reported activation energies for the propane aromatization,²³ the results obtained from this work are acceptable.

TABLE IV. Estimated kinetic parameters for propane aromatization reaction

α / h^{-1}	0.039±0.0013		
Reaction step j	$k_{j,0} / 10^3 \text{ mol}^{(1-P_j)} (\text{m}^3)^{P_j} \text{ g}^{-1} \text{ h}^{-1}$	$E_j / \text{kJ mol}^{-1}$	P_j
1	3.49±0.06	124.53±2.05	2.52±0.15
2	5.37±0.12	130.74±2.64	2.66±0.19
3	2.26±0.13	88.58±4.02	3.59±0.41
4	9.6±0.4	143.64±8.26	2.89±0.16
5	8.73±0.16	48.99±2.33	1.9±0.04
6	2.1±0.03	67.81±1.88	1.66±0.14

It has been shown by Baradaran *et al.*³⁵ that introducing of 0.4 wt. % Zn over HZSM-5 catalyst in the propane aromatization led to an increase in the deactivation constant from 0.0056 to 0.025 h^{-1} . By comparing the obtained deactivation constant value (Table IV) with Baradaran *et al.*³⁵ results, it can be concluded that the increasing of deactivation constant is due to the increase of Zn load from 0.4 to 3 wt. %. The results also indicate that with the increasing Zn amount in the HZSM-5 catalyst, the dehydrogenation and the conversion of naphthenes to aromatics increase, which can result in higher rate of coke formation. In accordance with the low coke formation, the low value of k for the reaction steps (4) and (6) can be expected (Table IV).

In order to validate the kinetic modeling, R^2 coefficient was used which should be between 0 and 1. Whatever the R^2 value is closer to 1 indicates a better fitness. R^2 coefficient, relative absolute error, RAE and root mean squared error, $RMSE$ were calculated by the following equations as shown in Table V:

$$SST = \sum_{s=1}^f (Y_{\text{exp},s} - \bar{Y}_{\text{exp}})^2 \quad (11)$$

$$SSE = \sum_{s=1}^f (Y_{\text{exp},s} - Y_{\text{model},s})^2 \quad (12)$$

$$R^2 = 1 - \frac{SSE}{SST} \quad (13)$$

$$RMSE = \sqrt{\frac{SSE}{f}} \quad (14)$$

$$RAE = \frac{1}{f} \sum_{s=1}^f \frac{|Y_{\text{exp},s} - Y_{\text{model},s}|}{Y_{\text{exp},s}} \quad (15)$$

Table V shows that according to the obtained R^2 , RAE and $RMSE$ values for the main products yield of paraffins, olefins and aromatics, the difference between the predicted and other experimental data is statistically insignificant.

TABLE V. R^2 , RAE and $RMSE$ values for main products yield

Yield of component	R^2	RAE	$RMSE$
Paraffins	0.96	0.10	0.62
Olefins	0.81	0.06	0.39
Aromatics	0.96	0.11	1.92

The Fig. 5 shows the scatter diagrams of the yields of paraffins, olefins and the aromatics. The predicted values of product yields by the kinetic model with other experimental data have been compared in Fig. 5. There are good agreements between the predicted values and the experimental data and the data points are distributed symmetrically on diagonal sides.

The mass fractions of lumps as a function of contact time at different temperatures and $TOS = 0.5$ h are shown in Fig. 6. The results show that the propane contact time influences the propane conversion and the product selectivity at the different temperatures. With an increase in the contact time, the yields of aromatics and paraffins enhances and the yield of olefins increases and then declines slightly. The produced heavy products were negligible. The observed decrease in the yield of olefins with the increase of the propane conversion and the yield of aromatics indicate that olefins (ethylene and propylene) are the primary intermediate products in the propane aromatization. The obtained trends in Fig. 6 are similar to the results of Roohollahi *et al.*²⁶ and Choudhary *et al.*³⁷

Fig. S-1 of the Supplementary material shows that the higher contact time leads to the higher propane conversion at different temperatures and times on stream. In addition, the decrease of the propane conversion is consistent with the decrease of temperature and the increase of time on stream.

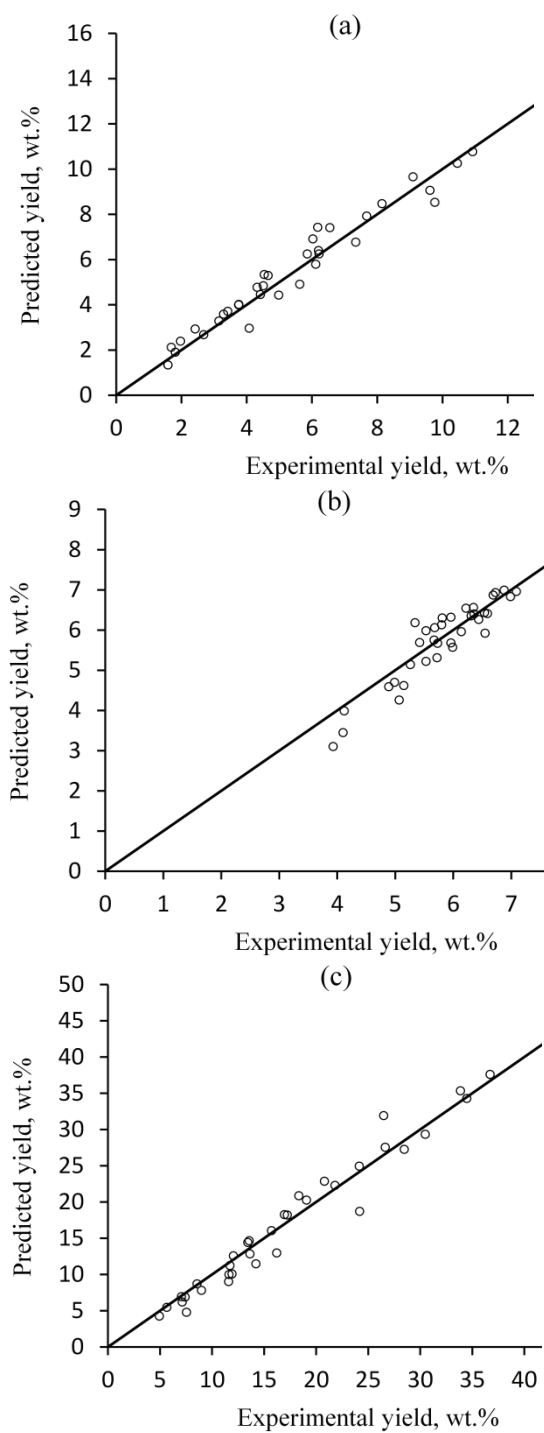


Fig. 5. Scatter diagram of the experimental and predicted: a) paraffins, b) olefins and c) aromatics yield.

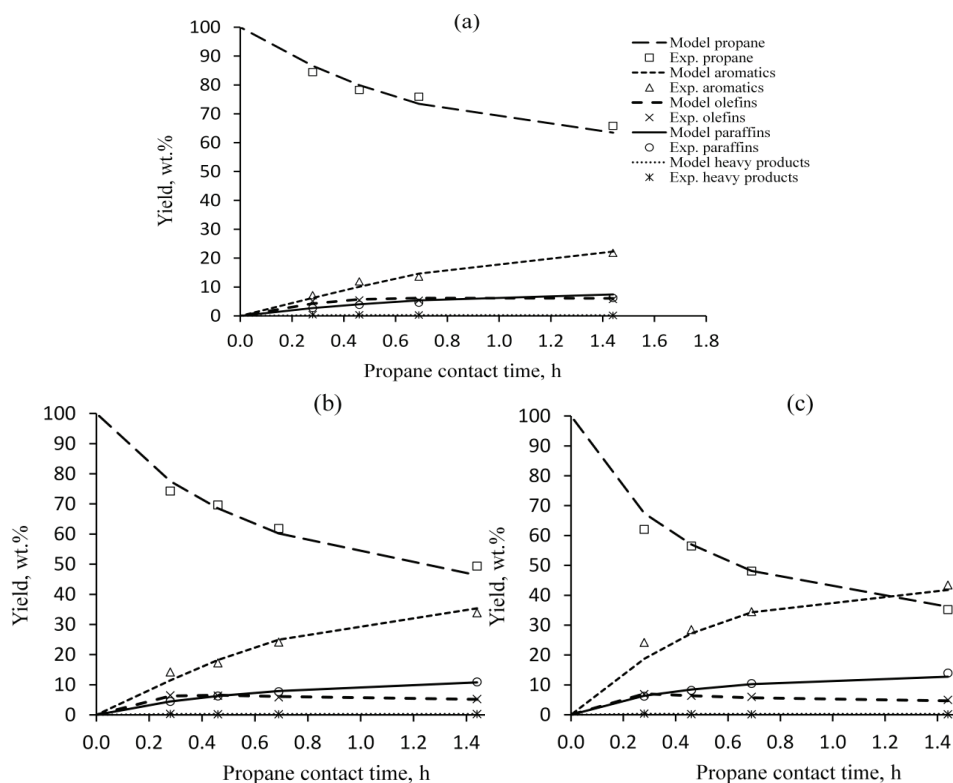


Fig. 6. Comparison between model predicted values (depicted as lines) and experimental data (depicted as symbols) for mass fractions of lumps at different contact times and $TOS = 0.5$ h; a) 500, b) 530 and c) 560 °C.

The main reactions in the propane aromatization process involve dehydrogenation, cracking and aromatization,³⁸ as given in the Supplementary material (Eqs. (S-8)–(S-10)).

According to the positive values of the enthalpy changes, these reactions are endothermic. Based on thermodynamic data, the endothermic reactions of the propane aromatization is favoured by the increasing temperature and consequently the products yield and propane conversion increase. The products yield as a function of temperature at propane contact time of 0.28 and 0.46 h are displayed in Fig. 7a and b, respectively. As the temperature increased, the yield of aromatics and paraffins went up and the yield of olefins increased insignificantly. The attained trends in Fig. 7 and the results of Choudhary *et al.*³⁸ are in a good agreement.

Fig. 8 provides the selectivity to aromatics as a function of time on stream at different temperatures and propane contact time of 0.69 h. As it can be seen, the

aromatics selectivity decreases by increasing the time on stream at different temperatures due to the coke deposition.

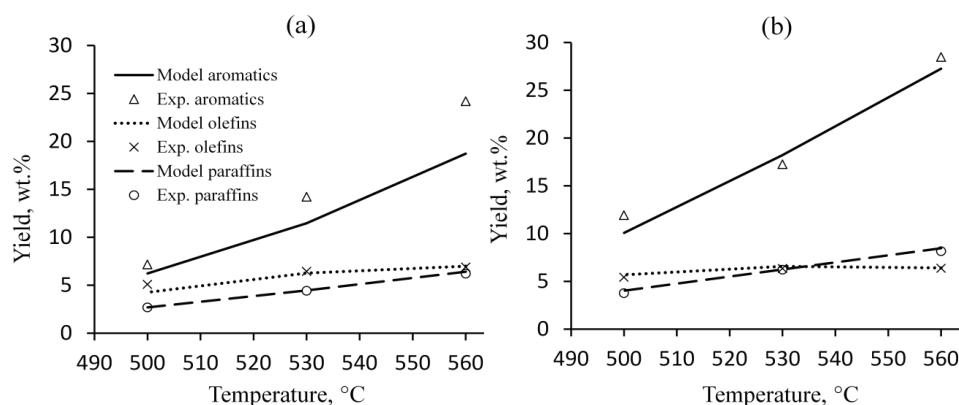


Fig. 7. Paraffins, olefins and aromatics yields as a function of temperature at $TOS = 0.5$ h, propane contact time of: a) 0.28 and b) 0.46 h.

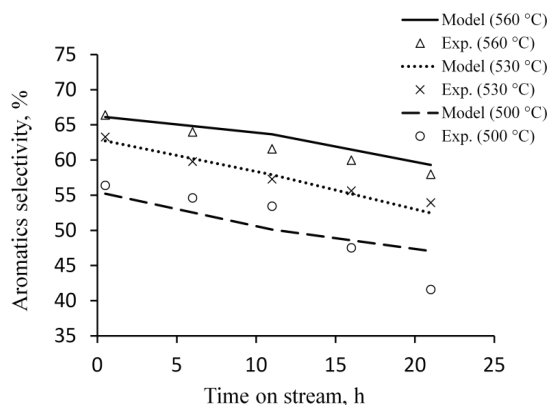


Fig. 8. Variation of aromatics selectivity with time on stream at different temperatures and propane contact time of 0.69 h.

Fig. 9 compares the evolution with time on stream (up to 21 h) of the experimental results and the model predicted main products yield at different temperatures and the propane contact time of 0.46 h. The results showed that by the increase of the time on stream and consequently the catalyst deactivation, because of coke deposition, the yields of paraffins and aromatics decreased, although the yield of olefins increased insignificantly. Therefore, the formed intermediate olefins could not completely convert to heavy products and aromatics. The goodness of fit in Fig. 9 shows the adequacy of the proposed deactivation model for predicting the evolution with time on stream of the main products yield. The obtained trends in Figs. 8 and 9 are close to the results reported in literature.³⁵

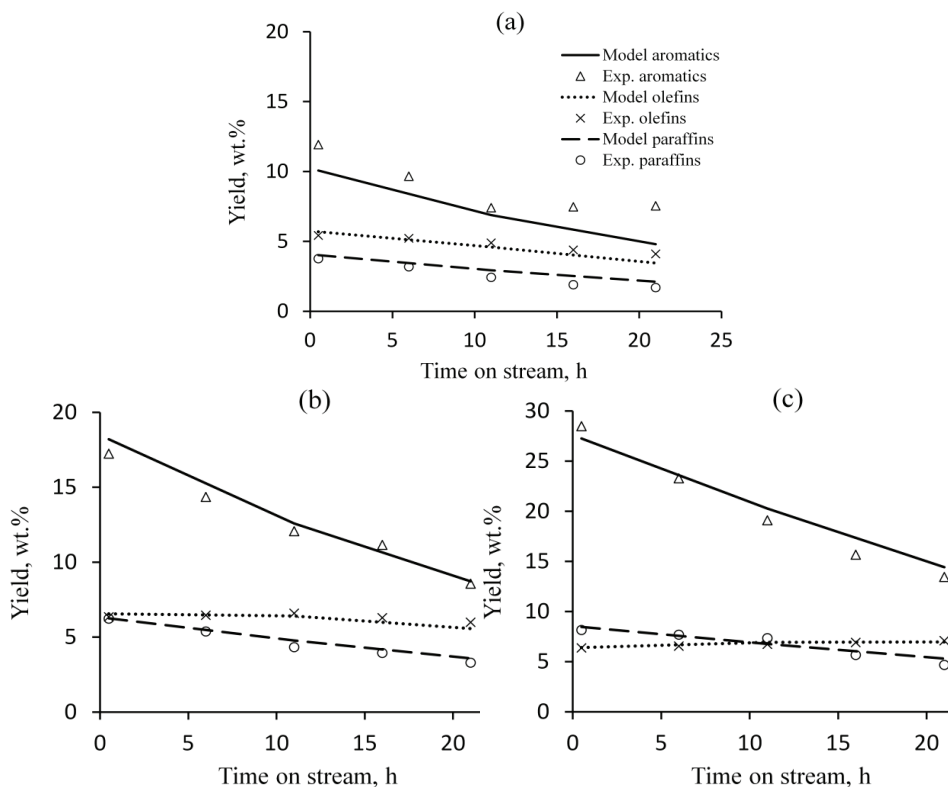


Fig. 9. Comparison of the evolution with time on stream of the experimental values (depicted as symbols) and model predicted values (depicted as lines) for main products yield at propane contact time = 0.46 h and a) 500, b) 530 and c) 560 °C.

CONCLUSION

The aromatization reactions of propane were studied on ZSM-5 catalyst and a lumped kinetic model, consisting of six lumped components and six reaction steps was developed. In the proposed model, the catalyst deactivation and the coke formation were considered and a simple exponential function was used for the catalyst deactivation model. Based on the estimated kinetic parameters, a good agreement between the experimental and the simulated mass fraction of lumps was attained.

According to the obtained power of the reaction species concentration values, second and third-order reactions have been suggested for the propane aromatization. A none-selective deactivation model was used considering the same simple deactivation kinetic equation for the estimation of the reaction rates of lumped components in the propane aromatization. The proposed model prediction of the propane conversion and the products distribution were satisfactory.

NOMENCLATURE

a	catalyst activity
b	number of lumps
c_i	concentration of lump i , mol m ⁻³
d	deactivation order
d_p	catalyst particles diameter, mm
d_r	reactor diameter, mm
DTA	differential thermal analysis
E_j	apparent activation energy of reaction step j , kJ mol ⁻¹
f	number of experimental runs
k_j	rate constant of reaction step j , mol ^(1-p) (m ³) ^p g ⁻¹ h ⁻¹
$k_{j,0}$	frequency factor of reaction step j , mol ^(1-p) (m ³) ^p g ⁻¹ h ⁻¹
L	reactor length, mm
m	mass flow rate of the feed, g h ⁻¹
M_i	average molecular weight of component i , mol g ⁻¹
n	number of reaction steps
P_j	power of the reaction species concentration j
R	universal gas constant, kJ mol ⁻¹ K ⁻¹
RAE	relative absolute error
R_i	reaction rate of lump i , mol g ⁻¹ h ⁻¹
r_j	rate of reaction step j , mol g ⁻¹ h ⁻¹
$RMSE$	root mean squared error
r_p	average pore radius, nm
S	mean crystallite size, μ m
S_{BET}	BET surface area, m ² g ⁻¹
SSE	sum of squared error
SST	total sum of squares
t	time on stream, h
T	temperature, K
TG	thermogravimetric
V_p	total pore volume, cm ³ g ⁻¹
W	catalyst weight, g
$WHSV$	weight hourly space velocity, h ⁻¹
w_i	mass fraction of compound i
Y	yield of products
<i>Greek symbols</i>	
α	catalyst deactivation constant, h ⁻¹
Ψ	non-separable deactivation function
τ	contact time, h
ν_j	stoichiometric coefficient of lump i in the reaction step j
ΔH_r°	heat of reaction, kJ mol ⁻¹
<i>Subscripts</i>	
A	propane
B	paraffins
C	olefins
D	heavy products
E	aromatics
F	coke

SUPPLEMENTARY MATERIAL

Chemical mechanisms, the obtained results for differently synthesized Zn/HZSM-5 catalysts and the effect of propane contact time on conversion at different temperatures and times on stream are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД

КИНЕТИЧКА СТУДИЈА АРОМАТИЗАЦИЈЕ ПРОПАНА ПОМОЋУ Zn/HZSM-5 ЗЕОЛИТА ПОД УСЛОВИМА КАТАЛИТИЧКЕ ДЕАКТИВАЦИЈЕ ПОМОЋУ ГЕНЕТИЧКОГ АЛГОРИТМА

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Изведена је кинетичка студија ароматизације пропана помоћу катализатора Zn/HZSM-5 на температури 500–560 °C и при брзини од 500–2500 cm³ g_{cat}⁻¹ h⁻¹ у про-точном реактору, под условима који доводе до деактивације катализатора. Предложен је сложени кинетички модел који се састоји од 6 компонената и 6 ступњева реакције, који би описао ароматизацију пропана. Он садржи 18 кинетичких параметара и константу деактивације катализатора. Фактори фреквенције и енергије активације ступњева у реакцији су одређени помоћу Аренијусове једначине. Експоненцијална функција времена је примењена на деактивацију катализатора и кинетички параметри су одређени помоћу генеричког алгоритма. Резултати су показали да је претпостављени сложени кинетички модел успешно приказао принос ароматизације пропана.

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REFERENCES

1. N. Al-Yassir, M. N. Akhtar, S. Al-Khattaf, *J. Porous Mater.* **19** (2012) 943
2. S. M. Al-Zahrani, *Dev. Chem. Eng. Mineral Process.* **6** (1998) 101
3. G. Caeiro, R. H. Carvalho, X. Wang, M. A. N. D. A. Lemos, F. Guisnet, F. Ramôa Ribeiro, *J. Mol. Catal., A: Chem.* **255** (2006) 131
4. A. A. Dergachev, A. L. Lapidus, *Russ. J. Gen. Chem.* **79** (2009) 1244
5. Y. Ono, *Catal. Rev.* **34** (1992) 179
6. C. Perego, P. Pollesel, in *Advances in Aromatics Processing Using Zeolite Catalysts*, E. Stefan, Ed., Elsevier, Amsterdam, 2010, p. 97
7. J. A. Biscardi, G.D. Meitzner, E. Iglesia, *J. Catal.* **179** (1998) 192
8. L. M. Lubango, M. S. Scurrall, *Appl. Catal., A: Gen.* **235** (2002) 265
9. A. Bhan, W. N. Delgass, *Catal. Rev.* **50** (2008) 19
10. V. R. Choudhary, K. Mantri, C. Sivadinarayana, *Microporous Mesoporous Mater.* **37** (2000) 1
11. A. Lapidus, V. Pavlova, N. Nekrasov, A. Dergachev, *Pet. Chem.* **50** (2010) 114
12. H. Krannila, W. O. Haag, B. C. Gates, *J. Catal.* **135** (1992) 115
13. J. A. Biscardi, E. Iglesia, *J. Catal.* **182** (1999) 117
14. M. Guisnet, N. Gnep, *Appl. Catal., A: Gen.* **146** (1996) 33
15. M. Guisnet, N. Gnep, F. Alario, *Appl. Catal., A: Gen.* **89** (1992) 1
16. L. H. Nguyen, T. Vazhnova, S.T. Kolaczkowski, D. B. Lukyanov, *Chem. Eng. Sci.* **61** (2006) 5881
17. D. B. Lukyanov, N. S. Gnep, M. R. Guisnet, *Ind. Eng. Chem. Res.* **34** (1995) 516

18. G. L. Price, V. Kanazirev, K. M. Dooley, V. I. Hart, *J. Catal.* **173** (1998) 17
19. V. R. Choudhary, C. Sivadinarayana, P. Devadas, S. D. Sansare, P. Magnoux, M. Guisnet, *Microporous Mesoporous Mater.* **21** (1998) 91
20. A. Matsuoka, S. Sakuma, M. Onodera, H. Kubota, *J. Porous Mater.* **20** (2013) 367
21. L. H. Nguyen, D. B. Lukyanov, *Petrovietnam J.* **6** (2011) 74
22. M. Guisnet, P. Magnoux, *Catal. Today* **36** (1997) 477
23. A. Bhan, S. H. Hsu, G. Blau, J. M. Caruthers, V. Venkatasubramanian, W. N. Delgass, *J. Catal.* **235** (2005) 35
24. G. Krishnamurthy, A. Bhan, W. N. Delgass, *J. Catal.* **271** (2010) 370
25. D. Mier, A. T. Aguayo, M. Gamero, A. G. Gayubo, J. Bilbao, *Ind. Eng. Chem. Res.* **49** (2010) 8415
26. G. Roohollahi, M. Kazemeini, A. Mohammadrezaee, R. Golhosseini, *AIChE J.* **58** (2012) 2456
27. M. Sedighi, K. Keyvanloo, J. Towfighi, *Fuel* **109** (2013) 432
28. M. Rahimpour, H. E. Behjati, *Fuel Process. Technol.* **90** (2009) 279
29. K. Keyvanloo, M. Sedighi, J. Towfighi, *Chem. Eng. J.* **209** (2012) 255
30. G. Mazloom, S. M. Alavi, *Reac. Kin. Mech. Catal.* **110** (2013) 387
31. J. A. Biscardi, E. Iglesia, *Catal. Today* **31** (1996) 207
32. Y. Zeinali, S. M. Alavi, *J. Serb. Chem. Soc.* **80** (2015) 355
33. A. G. Gayubo, A. Alonso, B. Valle, A. T. Aguayo, M. Olazar, J. Bilbao, *Chem. Eng. J.* **167** (2011) 262
34. P. Pérez-Uriarte, A. Ateka, A. G. Gayubo, T. Cordero-Lanzac, A. T. Aguayo, J. Bilbao, *Chem. Eng. J.* **311** (2017) 367
35. S. Baradaran, M. Sohrabi, P. Moghimpour Bijani, S. J. Royae, S. Sahebdehfar, *Can. J. Chem. Eng.* **93** (2015) 727
36. S. Sahebdehfar, M. T. Ravanchi, F. T. Zangeneh, S. Mehrazma, S. Rajabi, *Chem. Eng. Res. Des.* **90** (2012) 1090
37. V. R. Choudhary, P. Devadas, *J. Catal.* **172** (1997) 475
38. V. R. Choudhary, P. Devadas, *Microporous Mesoporous Mater.* **23** (1998) 231.